Chemical Reaction Engineering
Ch 10

Fall 2022

→ Combustion reaction

& saftey

Notes about Ch 10

- Do read the material in the text & the problems at the end of the chapter
  - Problems are realistic in many ways
  - Think about the problem case

1. Administrative → Policy & Protocol
2. Procedural → Standard operating Procedure
3. Engineering → ventilation, Fume hood, Clearance, chemical comp.
4. Personal Protective equipment (PPE) → PPE last design layer

googles, hard hat, steel toe shoes

IN WHAT WAYS DO WE NEED TO BE CONCERNED ABOUT SAFETY IN RXN ENGINEERING?

Safety

- Types of reactions
- Reaction operating conditions
- Variability of reactions & process
- Chemical species used
- Complexity of systems
- Reactor type

Important Note

- **Wearing gloves & goggles is the last line of protection, not the first!**
- **1) Designs**
  - Material of construction, wall thickness, concentrations and quantities, etc.
  - Inherently safe design
    - Auto-quenching as an example
- **2) Engineering controls**
  - Pressure reliefs
  - Blast shields
  - Containment dykes
  - Ventilation systems
- **3) Operating Procedures**
  - Management of Change procedures (MOC)
  - HAZOP analyses
- **4) Alarms & warnings**
- **5) Personal protective equipment**

Chain Reactions

- Generic Rxn

$A \rightarrow B + C$ Overall Rxn

$n_iA \rightarrow R\cdot$ Radical $r_i = k_i[C_A]^{ni}$

initiation step

$A + R\cdot \rightarrow B + C + R\cdot$ $r_p = k_p[C_A][C_R]$

propagation step(s)

$n_tR\cdot \rightarrow X$ $r_t = k_t[C_R]^{nt}$

termination step

Chain Reactions

- Propagation step can run indefinitely at rate r_p once initiated by r_i
- r_t terminates the reaction

Chain Reactions

- Activation of the chain reaction is generally dominated by the initiator
  - Frequently the E_i is high and E_p is low
- For the overall rxn:

$$E_{eff} = \frac{E_i}{n_t} - \frac{E_t}{n_t} + E_p$$

Chain Reactions

rxn: $A \rightarrow B + C$

- Overall Rate
  - Do PSSA on C_R
  - Get

$$r = \left(\frac{k_i}{n_t k_t}\right)^{1/n_t} k_p C_A^{1+n_i/nt} \quad \Bigg\}$$

Refer supplementary material for derivation

Example 10-1

- Consider the chain reaction

$A \rightarrow R^{\bullet}$ $\quad r_i = k_i C_A$

$A + R^{\bullet} \rightarrow B + C + R^{\bullet}$ $\quad r_p = k_p C_A C_R$

$R^{\bullet} \rightarrow X$ $\quad r_t = k_t C_R$

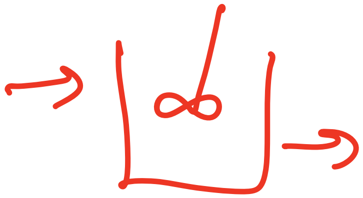
in a CSTR assuming constant density.

a) Write out the mass balance equations for A, B, R and X in a CSTR assuming constant density.

b) Find the overall reaction rate in terms of C_A

c) Find the residence time required for 90% conversion of A in a CSTR assuming PSSA if $C_{Ao} = 2.0$ M, $k_i = 0.0010$ sec^{-1}, $k_p = 20$ L/mol sec, $k_t = 0.10$ sec^{-1}.

d) What are C_R and C_X for this conversion?



$A \rightarrow R^\circ$ $\quad \textcircled{r_i}$ $\qquad r_i = k_i C_A$

$A + R^\circ \rightarrow B + C + R^\circ$ $\quad \textcircled{r_p}$ $\qquad r_p = k_p C_A C_R$

$R^\circ \rightarrow X$ $\quad \textcircled{r_t}$ $\qquad r_t = k_t C_R$

(a) Mass balances (For CSTR):

Ⓐ $\boxed{\dfrac{C_{A0} - C_A}{\tau} = r_A} = -r_i - r_p = -k_i C_A - k_p C_A C_R$

Ⓑ $\dfrac{C_B - \cancel{C_{B0}}^{\,0}}{\tau} = r_B = +r_p = \_\_\_\_$

Ⓒ $C_B = C_C$ $\quad\Big|\quad$ Ⓡ $\dfrac{C_R - \cancel{C_{R0}}^{\,0}}{\tau} = r_i - r_t$

Ⓧ $\dfrac{C_X - \cancel{C_{X0}}^{\,0}}{\tau} = r_t = k_t C_R$

(b) $r_{overall}$ in terms of C_A

$$r_{overall} = r_P = k_P C_A \underline{C_R}$$

PSSA on C_R: $\frac{dC_R}{dt} = 0 = k_i C_A - k_t C_R \Rightarrow \boxed{C_R = \frac{k_i}{k_t} C_A}$

$$\boxed{\therefore r_{overall} = \frac{k_P k_i}{k_t} C_A^2}$$

(similar to the result in slide 9)

(c) $X = 0.9$, $C_{A0} = 2\,M$, $\therefore C_A = 0.2\,M$

For CSTR: $\frac{C_{A0} - C_A}{\tau} = r_{overall} = \frac{k_P k_i}{k_t} C_A^2$

$$\therefore \tau = \frac{C_{A0} - C_A}{r_{overall}} = \frac{C_{A0} - C_A}{\frac{k_P k_i}{k_t} \cdot C_A^2} = \underline{\underline{225\ sec}}$$

(d) C_R & C_X for $x = 0.9$?

From mass bal: $\underline{R} \Rightarrow \dfrac{C_R}{\tau} = k_i C_A - k_t C_R$

$$\therefore C_R = \frac{\tau k_i C_A}{\tau k_t + 1} = \underline{\underline{0.002\,M}}$$

$\underline{X} \Rightarrow \dfrac{C_X}{\tau} = k_t C_R$

$$\therefore C_X = \tau k_t C_R = \underline{\underline{0.045\,M}}$$

$\underline{B} \Rightarrow C_B = \tau k_p C_A C_R = \underline{\underline{1.8\,M}}$

Examples of Chain Reactions?

- Polymerization
- Nuclear fission
- Acetaldehyde decomposition
- Autooxidations forming peroxides

Thermal Ignition

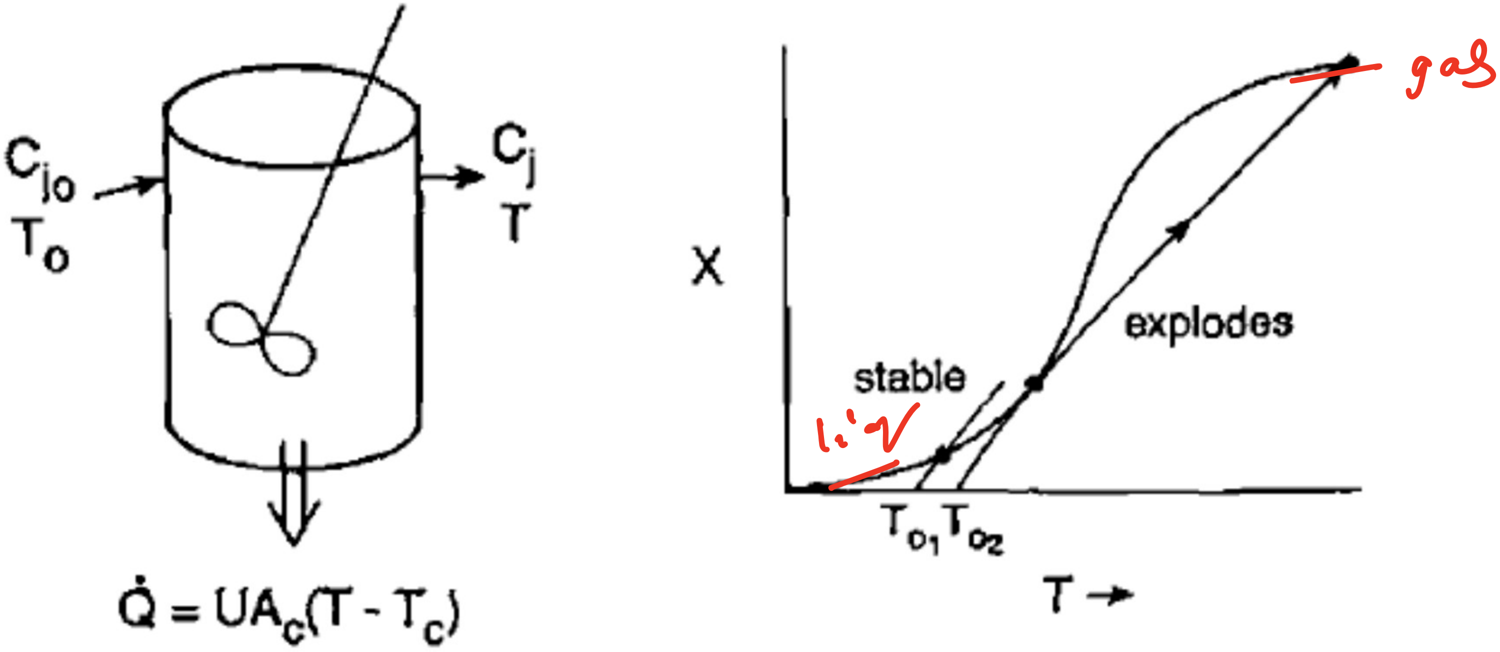


Figure 10–10 Heat generation and removal for combustion reaction in a CSTR. When the feed temperature increases slightly, the rate can go from nearly zero to nearly completion when the heat removal curve becomes tangent to the heat generation curve, and the steady-state temperature jumps to a high value. This simple model shows why these processes can be extremely sensitive to conditions such as size, heat transfer, and the temperature of surroundings.

Combustion Reactions

- **Also chain reactions**
- **Highest risk reactions commonly performed by chemical engineers**
  - **Highly exothermic**
  - **Can become very non-isothermal**
- **The temperatures and pressures generated during a runaway reaction can be catastrophic to the reactor vessel**
  - **Think back to the T and P calculations we did about the methane leak in the room**

What-Ifs

- **When we design a reactor we have to think about the "what-ifs"**
  - **Overfill/underfill reactor**
  - **Heat exchanger fails**
  - **Vessel leaks**
  - **Stirring stops**
  - **Reactor plugs**
  - **Wrong material fed to reactor**

Control Concerns

- Temperature
- Filling
- Flowrates
- Pressure

Material Hazards

- Many of the chemicals we work with are hazardous and have high risks
- We have to think about what would happen if a release occurred
  - Before anything happens
  - Too late if something already has happened

Material Hazards

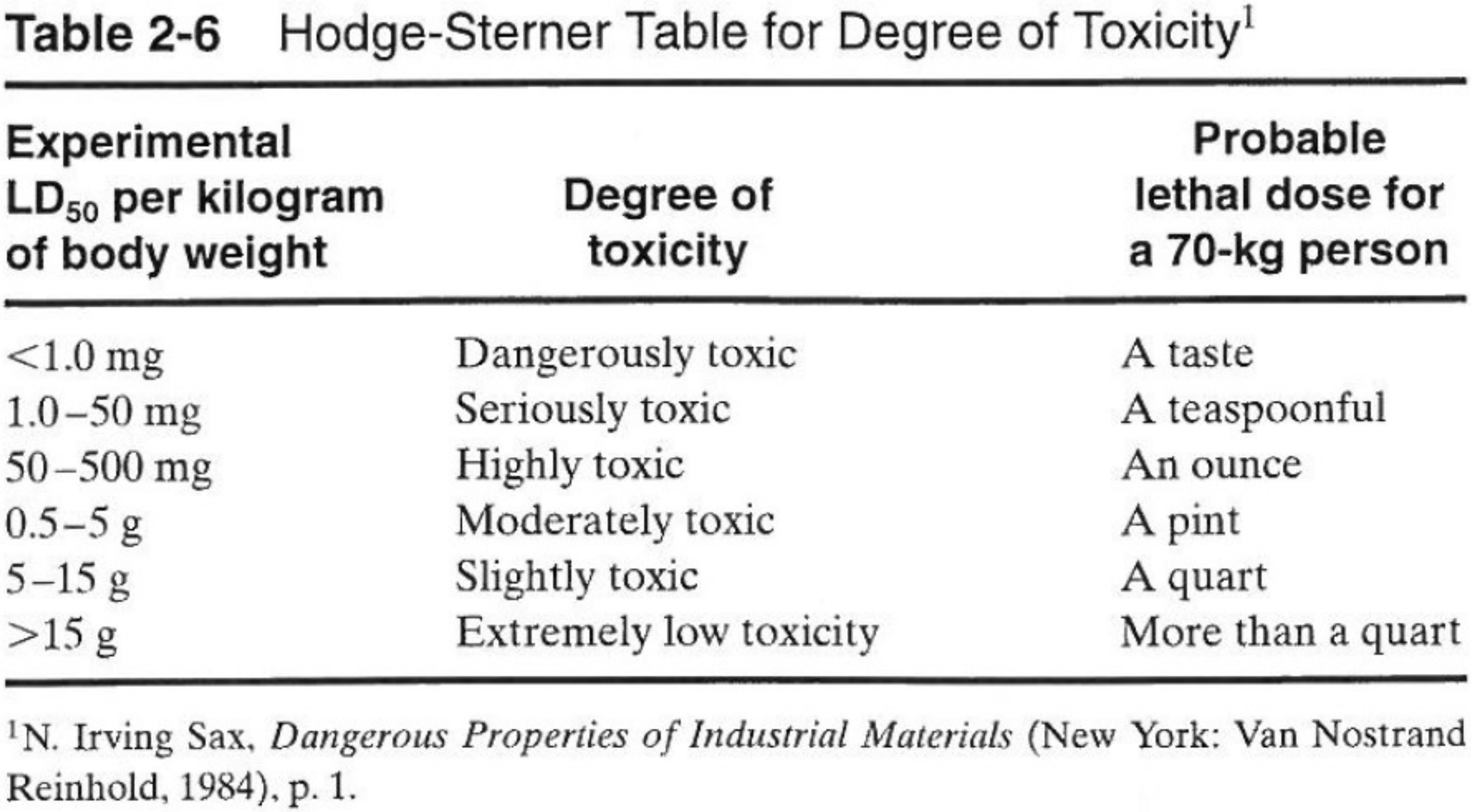


Table 2-6 Hodge-Sterner Table for Degree of Toxicity[1]

Experimental LD_{50} per kilogram of body weight	Degree of toxicity	Probable lethal dose for a 70-kg person
<1.0 mg	Dangerously toxic	A taste
1.0–50 mg	Seriously toxic	A teaspoonful
50–500 mg	Highly toxic	An ounce
0.5–5 g	Moderately toxic	A pint
5–15 g	Slightly toxic	A quart
>15 g	Extremely low toxicity	More than a quart

[1] N. Irving Sax, *Dangerous Properties of Industrial Materials* (New York: Van Nostrand Reinhold, 1984), p. 1.

Materials Hazards

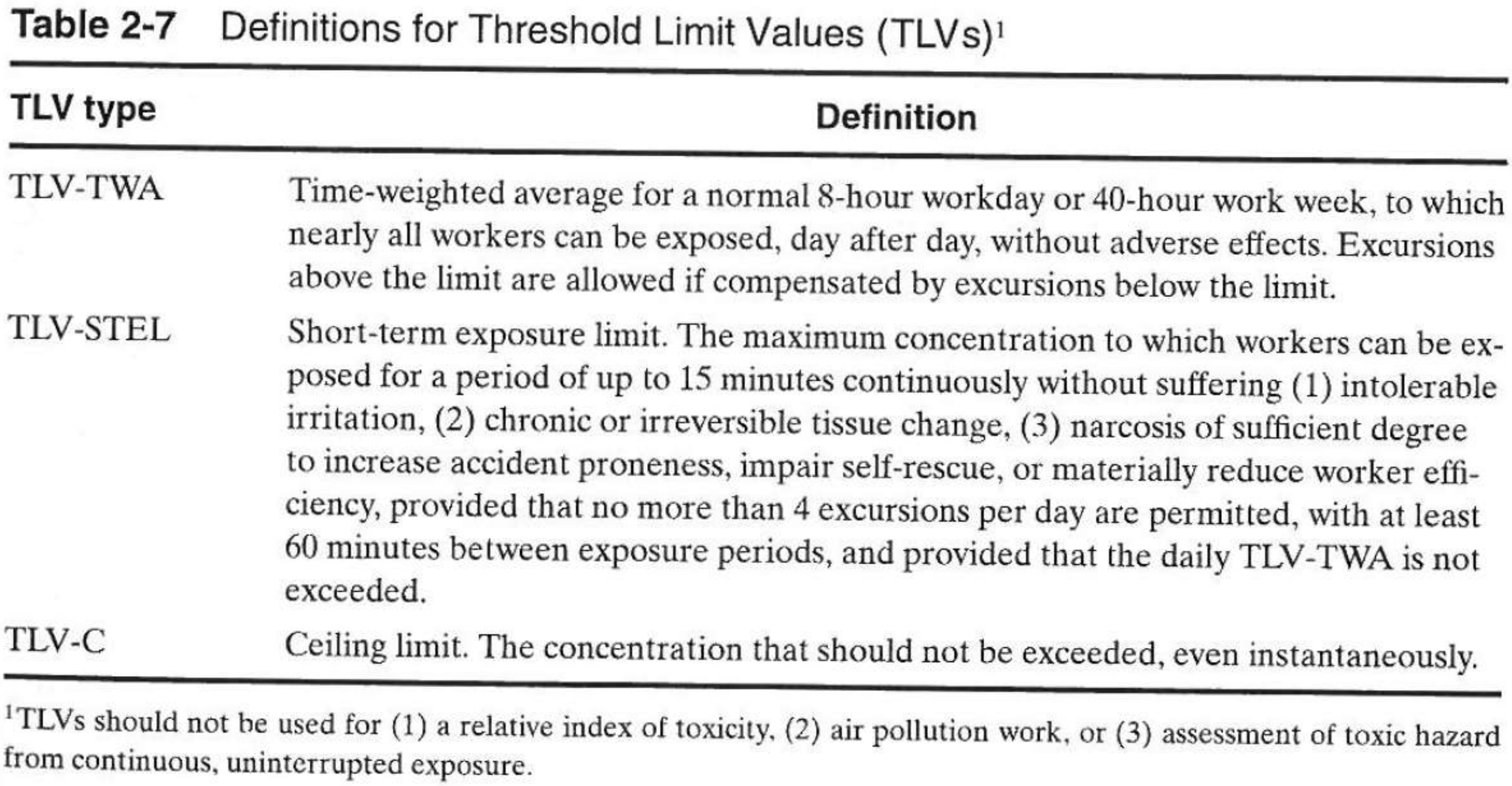


Table 2-7 Definitions for Threshold Limit Values (TLVs)[1]

TLV type	Definition
TLV-TWA	Time-weighted average for a normal 8-hour workday or 40-hour work week, to which nearly all workers can be exposed, day after day, without adverse effects. Excursions above the limit are allowed if compensated by excursions below the limit.
TLV-STEL	Short-term exposure limit. The maximum concentration to which workers can be exposed for a period of up to 15 minutes continuously without suffering (1) intolerable irritation, (2) chronic or irreversible tissue change, (3) narcosis of sufficient degree to increase accident proneness, impair self-rescue, or materially reduce worker efficiency, provided that no more than 4 excursions per day are permitted, with at least 60 minutes between exposure periods, and provided that the daily TLV-TWA is not exceeded.
TLV-C	Ceiling limit. The concentration that should not be exceeded, even instantaneously.

[1] TLVs should not be used for (1) a relative index of toxicity, (2) air pollution work, or (3) assessment of toxic hazard from continuous, uninterrupted exposure.

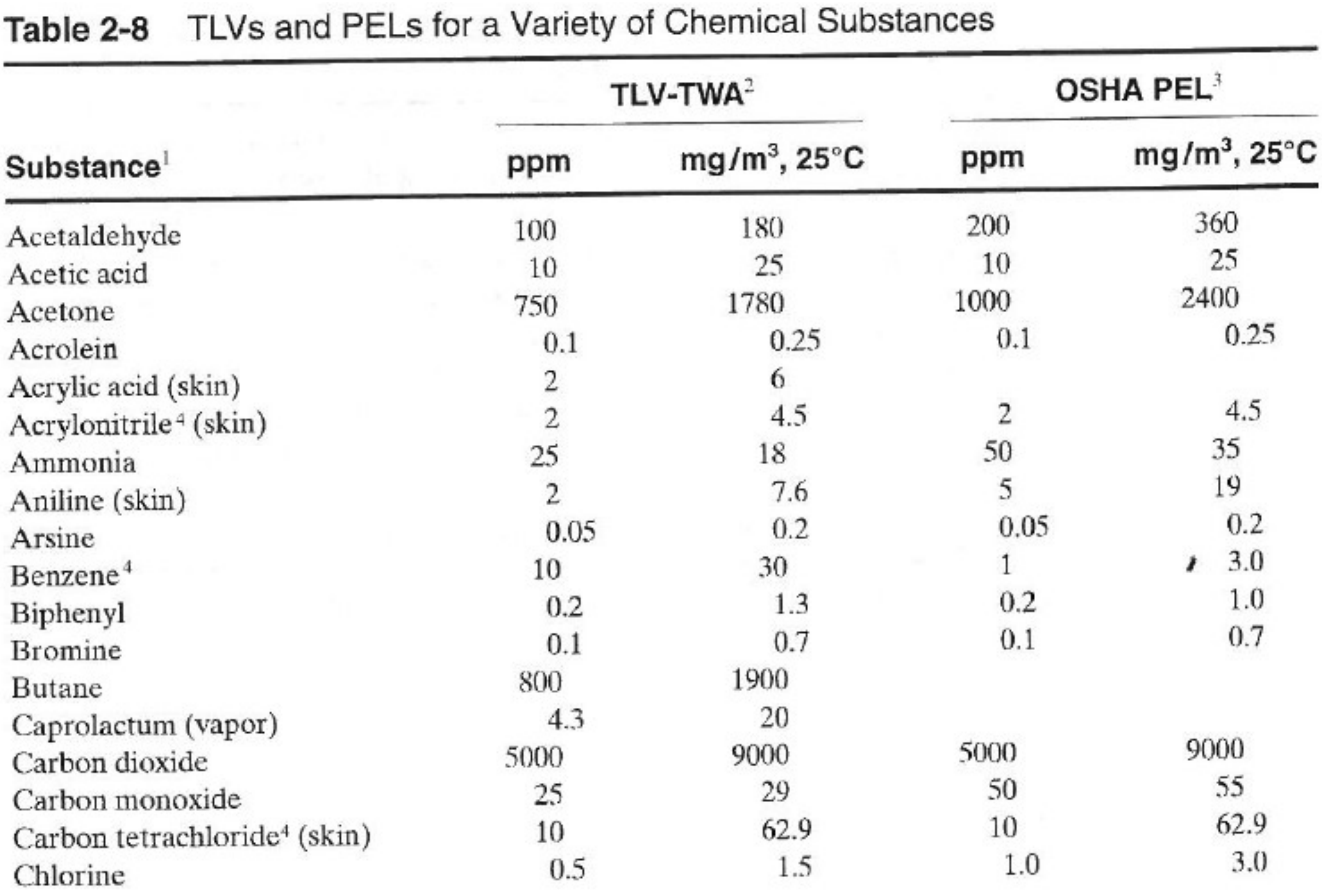


Table 2-8 TLVs and PELs for a Variety of Chemical Substances

	TLV-TWA[2]		OSHA PEL[3]	
Substance[1]	**ppm**	**mg/m^3, 25°C**	**ppm**	**mg/m^3, 25°C**
Acetaldehyde	100	180	200	360
Acetic acid	10	25	10	25
Acetone	750	1780	1000	2400
Acrolein	0.1	0.25	0.1	0.25
Acrylic acid (skin)	2	6		
Acrylonitrile[4] (skin)	2	4.5	2	4.5
Ammonia	25	18	50	35
Aniline (skin)	2	7.6	5	19
Arsine	0.05	0.2	0.05	0.2
Benzene[4]	10	30	1	3.0
Biphenyl	0.2	1.3	0.2	1.0
Bromine	0.1	0.7	0.1	0.7
Butane	800	1900		
Caprolactum (vapor)	4.3	20		
Carbon dioxide	5000	9000	5000	9000
Carbon monoxide	25	29	50	55
Carbon tetrachloride[4] (skin)	10	62.9	10	62.9
Chlorine	0.5	1.5	1.0	3.0

Reactor Design & Safety

- Reactor size
- Reactor material
- Wall thickness
- Temperature management
- Pressure relief
- Chemical components & intermediates

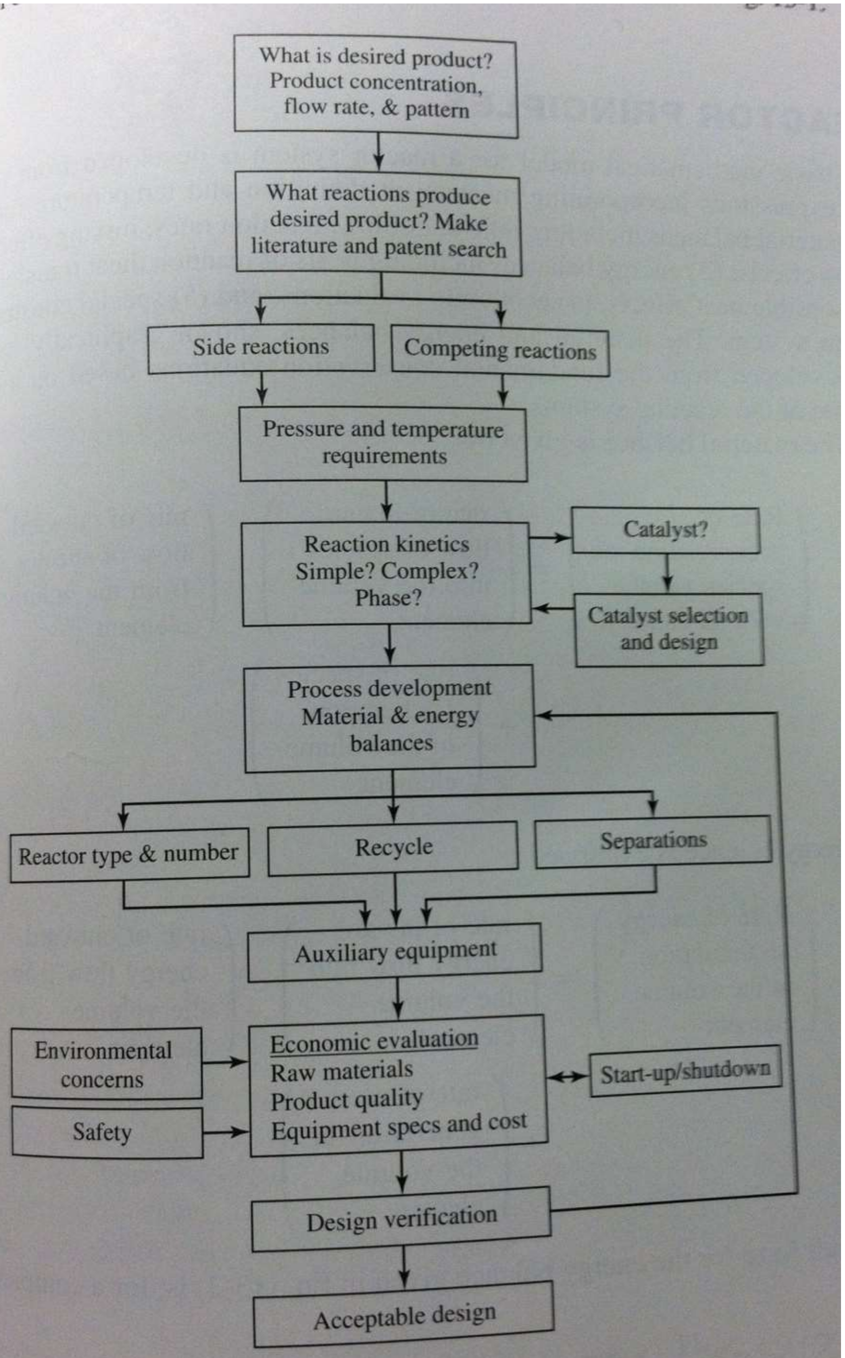
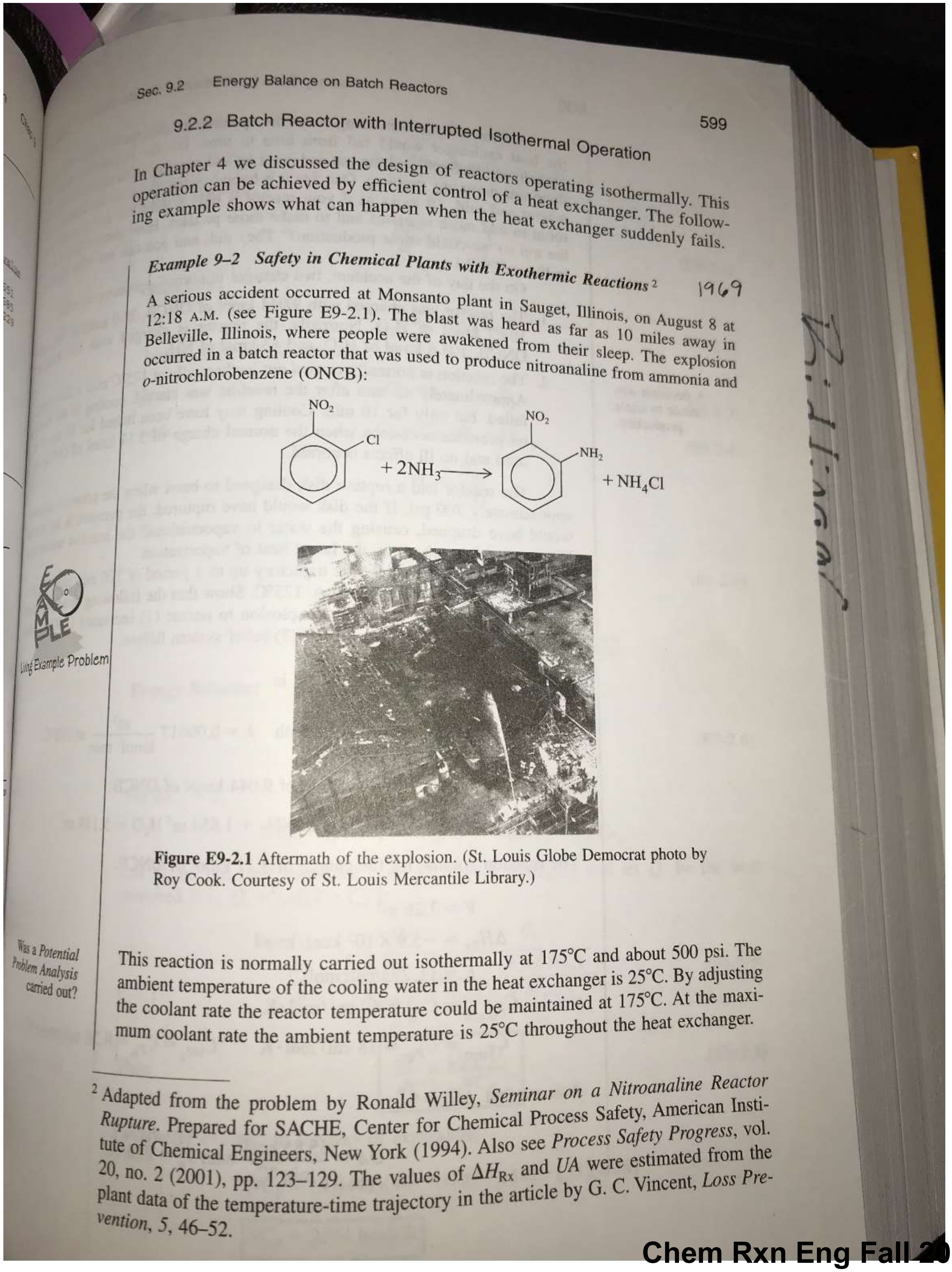


Figure 13-1
Reaction design and evaluation scheme flowchart

Peters, Timmerhaus
& West



Sec. 9.2 Energy Balance on Batch Reactors 599

9.2.2 Batch Reactor with Interrupted Isothermal Operation

In Chapter 4 we discussed the design of reactors operating isothermally. This operation can be achieved by efficient control of a heat exchanger. The following example shows what can happen when the heat exchanger suddenly fails.

Example 9–2 ***Safety in Chemical Plants with Exothermic Reactions***[2] 1969

Living Example Problem

A serious accident occurred at Monsanto plant in Sauget, Illinois, on August 8 at 12:18 A.M. (see Figure E9-2.1). The blast was heard as far as 10 miles away in Belleville, Illinois, where people were awakened from their sleep. The explosion occurred in a batch reactor that was used to produce nitroanaline from ammonia and *o*-nitrochlorobenzene (ONCB):

Figure E9-2.1 Aftermath of the explosion. (St. Louis Globe Democrat photo by Roy Cook. Courtesy of St. Louis Mercantile Library.)

Was a Potential Problem Analysis carried out?

This reaction is normally carried out isothermally at 175°C and about 500 psi. The ambient temperature of the cooling water in the heat exchanger is 25°C. By adjusting the coolant rate the reactor temperature could be maintained at 175°C. At the maximum coolant rate the ambient temperature is 25°C throughout the heat exchanger.

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[2] Adapted from the problem by Ronald Willey, *Seminar on a Nitroanaline Reactor Rupture*. Prepared for SACHE, Center for Chemical Process Safety, American Institute of Chemical Engineers, New York (1994). Also see *Process Safety Progress*, vol. 20, no. 2 (2001), pp. 123–129. The values of ΔH_{Rx} and UA were estimated from the plant data of the temperature-time trajectory in the article by G. C. Vincent, *Loss Prevention*, 5, 46–52.

Monsanto Explosion, Sauget, Illinois

(Fogler, Elements of Chemical Reaction Engineering, 4th ed)